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Simple CVM-based approximations for the configurational entropy

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Abstract. – It is shown how to derive simple polynomial expressions for the variational configurational entropy starting from the cluster variation method (CVM). As an example, first six terms of the expansion of the entropy in powers of the nearest-neighbour (NN) short-range order (SRO) parameter are obtained for the NN Ising ferromagnet on the face-centered cubic lattice using the tetrahedron (T-CVM) approximation. Calculated values of the transition temperature and the NN SRO parameter at the transition converge rapidly to their T-CVM counterparts as order of the approximation increases.

The cluster variation method (CVM) proposed originally by Kikuchi [1] and later reformulated, further developed and applied to a broad range of problems by many authors (for reviews, see [2]-[4]), is at present a standard and well-established technique for quantitative calculations of finite-temperature properties of systems undergoing order-disorder transitions. The CVM is essentially a procedure for obtaining approximate analytical expressions for the variational configurational entropy S. The CVM entropy is written in terms of probabilities of finding various possible atomic (spin) configurations on lattice clusters belonging to some basic, or maximal, cluster. A particular CVM approximation for the entropy is therefore defined by the choice of the basic cluster. The second necessary ingredient, the internal energy E, is the statistical average of the Hamiltonian of the problem, and is a function of the same (or related) variables as the entropy. The resulting variational free energy $F = E - TS$ (T is the absolute temperature) is then minimized with respect to all configurational parameters. This can be done using probabilities which correspond to the basic cluster. However, they are not independent, since the sum of the probabilities of all possible configurations on the basic cluster is equal to unity. This condition is explicitly taken into account during the minimization; the obtained equations can then be solved by means of the natural iteration method of Kikuchi [5].

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Alternatively, the set of independent variables (spin averages) is chosen [6]. The value of F at the minimum coincides with the actual approximate free energy of the system.

Being a reliable and widely used theoretical tool, the CVM at the same time has certain disadvantages. One of them is that the CVM approximations for the entropy are fairly complicated, especially for comparatively large basic clusters, and the number of independent variational parameters in the expression for F becomes progressively large with the increasing size of the basic cluster. As a result, the method is intrinsically numerical. The aim of the present study is to simplify the CVM thermodynamic treatment and find suitable formulae for the configurational entropy, thus making the variational free energy more tractable analytically. The general description of the proposed approach is followed by a particular, relatively simple example of the nearest-neighbour (NN) Ising ferromagnet on the face-centered cubic (FCC) lattice in the tetrahedron (T-CVM) approximation and by a preliminary test of the results obtained in this example case.

We start from the exposition of the general idea leading to the simplification of the CVM. In what follows the Ising language is used, and the variational free energy is minimized with respect to the spin averages which are independent configurational parameters; all relevant cluster probabilities can be expressed in terms of these spin averages. The free energy thus depends on interactions v_n (including the magnetic field) and spin averages ξ_n. The equilibrium values of ξ_n are determined from the minimization conditions

$$\frac{\partial F}{\partial \xi_n} = 0. \tag{1}$$

The possibility of the CVM simplification proposed here is based on the fact that in most CVM approximations the configurational entropy contains significantly more minimization parameters ξ_n than the internal energy. The latter is the statistical average of the Hamiltonian

$$H = \sum_n v_n a_n, \tag{2}$$

where a_n are some operators. In the theory of ordering these operators are products of the spin variables. The averages φ_n of operators a_n form a subset of the set $\{\xi_n\}$. All other spin averages are denoted as χ_n. The internal energy then depends on v_n and φ_n, while the entropy is a function of the spin averages only, but depends on both φ_n and χ_n:

$$E = E(\{v_n\}, \{\varphi_n\}) = \sum_n v_n \varphi_n, \quad S = S(\{\varphi_n\}, \{\chi_n\}). \tag{3}$$

Eqs. (1) now become

$$\frac{\partial S}{\partial \varphi_n} = \frac{v_n}{T}\ , \quad \frac{\partial S}{\partial \chi_n} = 0\ . \tag{4}$$

It is seen that the minimization of the free energy with respect to the spin averages χ_n reduces to the maximization of the entropy. Corresponding equations are simply the relations between different configurational parameters, since they contain no information about interactions in the system, and as such can be taken into account in the CVM entropy from the very beginning (for a given Hamiltonian and a given thermodynamic phase). They can be used to find the spin averages χ_n as functions of the spin averages φ_n. The results are then substituted into the entropy, thus expressing it in terms of φ_n. The resulting variational free energy also depends only on the spin averages φ_n conjugated to the interactions v_n. The number of remaining independent variational parameters is greatly reduced in comparison with the original CVM treatment; in particular, it is equal to the total number of distinct interactions, if all lattice

sites are equivalent (*i.e.*, when there are no sublattices). In the widely used case of pairwise interactions this approach leads to the variational free energy which is a function of the point and pair spin averages.

In itself the outlined approach is not very useful, since equations to be solved are usually rather complicated, and so would be the final expression for the entropy. This difficulty can be overcome by defining another set of parameters, the cumulants of the remaining spin averages φ_n, and seeking the solutions of these equations (*i.e.*, the expressions for the spin averages χ_n) in the form of series expansions in powers of the cumulants of the pair and higher-order spin averages φ_n. These expansions are then substituted into the CVM approximation for the entropy, and the entropy itself is also expanded in powers of the same parameters. The cumulants of the spin averages are defined as follows: the cumulant average of a product of n spin variables is the nth-order residue when all combinations of cumulant averages of lower order are subtracted from the actual average of the product. In other words,

$$\begin{gathered}\langle s_i\rangle = \langle s_i\rangle_c\,, \quad \langle s_i s_j\rangle = \langle s_i\rangle_c \langle s_j\rangle_c + \langle s_i s_j\rangle_c\,, \\ \langle s_i s_j s_k\rangle = \langle s_i\rangle_c \langle s_j\rangle_c \langle s_k\rangle_c + \langle s_i s_j\rangle_c \langle s_k\rangle_c + \langle s_i s_k\rangle_c \langle s_j\rangle_c + \langle s_j s_k\rangle_c \langle s_i\rangle_c + \langle s_i s_j s_k\rangle_c\,, \end{gathered} \tag{5}$$

etc. [7]. Here s_i is a spin variable attributed to the lattice site i, $\langle\rangle_c$ denotes the cumulant average, and $\langle\rangle$ is the usual statistical average. By retaining first several terms in the expansion for the entropy a sufficiently simple polynomial approximation to the (already approximate) CVM expression is obtained. The cumulants used as expansion parameters are almost always sufficiently small to justify the expansion; the irreducible pair correlation function, whose matrix elements are the cumulants of the pair averages and are proportional to the corresponding short-range order (SRO) parameters, can serve as an example. The coefficients of the polynomial are functions of the point averages. The cumulants of the point averages are these averages themselves, *i.e.*, the site magnetizations; they cannot be used as expansion parameters, since they are not necessarily small (*e.g.*, in the ordered phase or in the case of sufficiently strong magnetic field above the transition).

To illustrate the proposed approach, we consider the tetrahedron version of the CVM for the ferromagnetic FCC Ising model with NN pair interactions. In the T-CVM approximation the variational configurational entropy is (see, *e.g.*, [5] or first of the reviews [2])

$$\begin{aligned}(Nk_B)^{-1}S \;=\; & -5\left(P^u \ln P^u + P^d \ln P^d\right) + 6\left(P^{uu} \ln P^{uu} + 2P^{ud} \ln P^{ud}\right. \\ & \left. + P^{dd} \ln P^{dd}\right) - 2\left(P^{uuuu} \ln P^{uuuu} + 4P^{uuud} \ln P^{uuud}\right. \\ & \left. + 6P^{uudd} \ln P^{uudd} + 4P^{uddd} \ln P^{uddd} + P^{dddd} \ln P^{dddd}\right). \end{aligned} \tag{6}$$

Here superscripts "u" and "d" stand for spins up and down, N is the number of lattice sites, and k_B is the Boltzmann constant. The entropy is expressed in terms of probabilities P of one-, two- and four-spin configurations on the basic cluster – the NN tetrahedron. As was mentioned before, not all of the probabilities in eq. (6) are independent. The set of independent parameters consists of four spin averages

$$\xi_1 = \langle s_i\rangle = m, \quad \xi_2 = \langle s_i s_j\rangle\,, \quad \xi_3 = \langle s_i s_j s_k\rangle\,, \quad \xi_4 = \langle s_i s_j s_k s_l\rangle\,, \tag{7}$$

where m is the magnetization and all lattice sites are nearest neighbours. The probabilities in eq. (6) are statistical averages of the corresponding products of occupation numbers which are linearly related to the spin variables [2]-[4], and thus can be expressed in terms of averages (7):

$$\begin{gathered} 2P^u = 1 + m, \quad 2P^d = 1 - m, \\ 4P^{uu} = 1 + 2m + \xi_2, \quad 4P^{dd} = 1 - 2m + \xi_2, \quad 4P^{ud} = 1 - \xi_2, \\ 16P^{uuuu} = 1 + 4m + 6\xi_2 + 4\xi_3 + \xi_4, \quad 16P^{dddd} = 1 - 4m + 6\xi_2 - 4\xi_3 + \xi_4, \end{gathered}$$

$$16P^{uuud} = 1 + 2m - 2\xi_3 - \xi_4,\ 16P^{uddd} = 1 - 2m + 2\xi_3 - \xi_4,\ 16P^{uudd} = 1 - \xi_2 + \xi_4. \quad (8)$$

The Hamiltonian of the Ising model is

$$H = -\frac{1}{2}\sum_{ij} J_{ij} s_i s_j - h\sum_i s_i \quad (9)$$

(J_{ij} is the exchange integral equal to $J > 0$ for NN sites and to zero otherwise, and h is the magnetic field), so that only first two averages (7) enter the expression for the internal energy,

$$N^{-1}E = -\frac{1}{2}ZJ\xi_2 - h\xi_1, \quad (10)$$

where Z is the NN coordination number. As a result, the set $\{\xi_n\}$ contains four averages, while its subset $\{\varphi_n\}$ consists of two variables ξ_1 and ξ_2. The minimization of the free energy with respect to ξ_3 and ξ_4 reduces to the maximization of the entropy with respect to these two variables and leads to the following equations:

$$P^{uuuu}\left(P^{uddd}\right)^2 = P^{dddd}\left(P^{uuud}\right)^2, \quad P^{uuuu}P^{dddd}\left(P^{uudd}\right)^6 = \left(P^{uuud}P^{uddd}\right)^4. \quad (11)$$

From eqs. (11) the averages ξ_3 and ξ_4 can be found as functions of the averages ξ_1 and ξ_2. According to the proposed general scheme, ξ_3 and ξ_4 should be sought as series expansions in powers of the cumulant of the pair average ξ_2. This cumulant is the NN matrix element of the irreducible pair correlation function. However, a quantity proportional to it, the NN SRO parameter α, is more often used. The relation between ξ_2 and α is

$$\xi_2 = m^2 + (1 - m^2)\alpha. \quad (12)$$

By iteratively solving eqs. (11) first six terms of the series expansions in powers of α for the spin averages ξ_3 and ξ_4 were found,

$$\xi_3 = a_0 + a_1\alpha + a_2\alpha^2 + a_3\alpha^3 + a_4\alpha^4 + a_5\alpha^5 + a_6\alpha^6 + O(\alpha^7), \quad (13)$$

$$\xi_4 = b_0 + b_1\alpha + b_2\alpha^2 + b_3\alpha^3 + b_4\alpha^4 + b_5\alpha^5 + b_6\alpha^6 + O(\alpha^7), \quad (14)$$

where the coefficients a_n and b_n are

$$\begin{gathered}
a_0 = m^3, \quad a_1 = 3m\left(1 - m^2\right), \quad a_2 = -6m\left(1 - m^2\right), \\
a_3 = 2m\left(5 - 9m^2\right), \quad a_4 = -6m\left(1 - 9m^2\right), \quad a_5 = -54m\left(1 - m^2\right), \\
a_6 = 2m\left(1 - m^2\right)^{-2}\left(185 - 1491m^2 + 3051m^4 - 1809m^6\right), \\
b_0 = m^4, \quad b_1 = 6m^2\left(1 - m^2\right), \quad b_2 = 3\left(1 - m^2\right)\left(1 - 9m^2\right), \\
b_3 = -8\left(1 - 15m^2 + 18m^4\right), \quad b_4 = 24\left(1 - 19m^2 + 36m^4\right), \\
b_5 = -24\left(1 - m^2\right)^{-1}\left(3 - 70m^2 + 267m^4 - 216m^6\right), \\
b_6 = 8\left(1 - m^2\right)^{-2}\left(26 - 691m^2 + 4089m^4 - 6993m^6 + 3537m^8\right). \quad (15)
\end{gathered}$$

Note that the expressions for the first four coefficients a_n and b_n coincide with the exact results obtained in the case of arbitrary pairwise interactions on the FCC lattice [8]. The tetrahedron CVM therefore correctly reproduces exact expansions for the averages ξ_3 and ξ_4 up to at least third order in α; exact formulae for the higher-order coefficients are at present unavailable. Substitution of the expansions (13) and (14) into the original T-CVM formula (6) and subsequent expansion of the entropy in powers of α gives

$$S = S_0 + S_1, \quad (16)$$

$$(Nk_B)^{-1}S_0 = -\left(\tfrac{1+m}{2}\ln\tfrac{1+m}{2} + \tfrac{1-m}{2}\ln\tfrac{1-m}{2}\right), \tag{17}$$

$$(Nk_B)^{-1}S_1 = c_2\alpha^2 + c_3\alpha^3 + c_4\alpha^4 + c_5\alpha^5 + c_6\alpha^6 + O(\alpha^7), \tag{18}$$

$$c_2 = -3, \quad c_3 = 4\left(1-m^2\right)^{-1}\left(2-m^2\right), \quad c_4 = -0.5\left(1-m^2\right)^{-2}\left(37-66m^2+45m^4\right),$$

$$c_5 = 4.8\left(1-m^2\right)^{-3}\left(10-39m^2+52m^4-19m^6\right),$$

$$c_6 = -0.2\left(1-m^2\right)^{-4}\left(641-3900m^2+7870m^4-6220m^6+1865m^8\right). \tag{19}$$

As expected, the entropy is a sum of two terms, the mean-field (Bragg-Williams) approximation (MFA) contribution S_0 and the correlation entropy S_1. The mean-field part of the entropy is the zero-order term, the linear term vanishes, since the entropy is maximal in the case of uncorrelated spins, and the expansion of the correlation entropy starts from the quadratic term. Now the variational free energy is a very simple function of only two parameters m and α (instead of four variables (7)). The equilibrium values of these two parameters are the solutions of two minimization equations,

$$\frac{\partial F}{\partial m} = 0\ , \quad \frac{\partial F}{\partial \alpha} = 0\ . \tag{20}$$

The obtained result (18) for the correlation entropy has especially simple form in the disordered phase with zero magnetic field. In this case first of eqs. (20) leads to the vanishing magnetization, while second gives α as a function of a single parameter – the normalized temperature $t = k_BT/ZJ$; the expansion (18) has numeric coefficients:

$$(Nk_B)^{-1}S_1 = -3\alpha^2 + 8\alpha^3 - 18.5\alpha^4 + 48\alpha^5 - 128.2\alpha^6 + O(\alpha^7)\ . \tag{21}$$

In the polynomial approximations for the entropy which can be obtained from the expansion (18) by retaining finite number of terms, the highest-order term must always be the even-order one. Otherwise, from the positiveness of the third- and fifth-order coefficients in the expansion (21) it follows that in the disordered phase the approximate entropy does not decrease monotonically with increasing positive α, but has a minimum at some α value and begins to increase afterwards. As a result, the solution of the second of eqs. (20) disappears as temperature decreases, while at higher temperatures this equation has two solutions instead of one. On the other hand, all calculated even-order coefficients are negative, and no such difficulties occur. As a preliminary test of the expansion (18) for the correlation entropy and related approximations for the variational free energy obtained in the present study, we calculate the normalized transition temperature t_c and the NN SRO parameter at the transition point α_c. The transition temperature is defined by the condition $\partial^2 F/\partial m^2 = 0$, together with the minimization equations (20). Values of t_c and α_c calculated in the three available (second-, fourth- and sixth-order) approximations are given in Table I. They clearly converge to the original T-CVM values, from above for t_c and from below for α_c; for instance, the overestimation of t_c changes from 20% in the MFA to 9% in the quadratic approximation, and then to 3% in the highest (sixth-order) approximation.

In summary, we have proposed the method of obtaining simple polynomial approximations for the variational configurational entropy which is based on the widely used CVM. This method utilizes the fact that the CVM entropy usually depends on much greater number of variational parameters than the internal energy. The minimization of the free energy with respect to variables which do not enter the expression for the internal energy is thus equivalent to the maximization of the entropy. The corresponding equations do not contain any information about the Hamiltonian of the system and play the role of constraints relating different variational parameters. They are used for the elimination of the redundant variables. The number of the remaining independent variational parameters in the free energy is almost

TABLE I. – *Normalised transition temperature $t_c = k_B T_c/ZJ$ and the NN SRO parameter at this temperature $\alpha_c = \alpha(t_c)$ in the three approximations for the variational free energy obtained from expansion (18) for the correlation entropy. The MFA and T-CVM values, as well as corresponding ratios, are also shown for the purpose of comparison. Results for the transition temperature can be further compared with the best known value $t_c = 0.81638$ [2].*

Approximation	t_c	t_c/t_c^{T-CVM}	α_c	$\alpha_c/\alpha_c^{T-CVM}$
MFA (0th order)	1	1.197	0	0
2nd order	0.90825	1.087	0.09175	0.459
4th order	0.87703	1.050	0.13930	0.697
6th order	0.86205	1.032	0.16304	0.815
T-CVM	0.83545	1	0.20000	1

always significantly reduced in comparison with the CVM. In the case of the absence of sublattices in the system it is equal to the total number of different interactions in the Hamiltonian (the magnetic field included). In practice this programme is implemented by using the expansion in powers of the cumulants of the remaining pair and higher-order spin averages: (i) the variables to be eliminated are found from the constraint equations as the corresponding series, (ii) the results are substituted into the initial CVM formula for the entropy, (iii) the obtained expression for the entropy is also expanded into the same series and (iv) finite number of terms in this expansion is retained. The resulting approximate free energy is a polynomial in the cumulants of the pair and higher-order spin averages conjugated to the interactions, *i.e.*, present in the expression for the internal energy. The coefficients of the polynomial are functions of the (sub)lattice magnetization(s). The final expression for the free energy always has the same functional form, regardless of the particular CVM approximation used initially for the configurational entropy; only the coefficients of the polynomial change. The evolution of these coefficients with the version of the CVM is a matter of considerable interest and will be the subject of a separate study. As a particular example, the ferromagnetic FCC Ising model with NN pair interactions in the tetrahedron approximation has been considered. First six terms of the expansion of the configurational entropy in powers of the NN SRO parameter have been obtained. Calculated values of the transition temperature and the NN SRO parameter at this temperature rapidly converge to the corresponding original T-CVM results with the increasing order of the approximation. The detailed study of the applicability and accuracy of the obtained approximations for the free energy is in progress and will be published elsewhere.

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